# A Versatile Low-Cost Approach to Dynamic Light Scattering

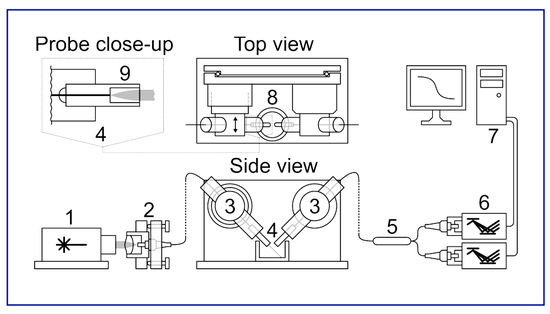
Denis Pristinski and Thomas Q. Chastek

Polymers Division, National Institute of Standards and Technology, Gaithersburg MD

## Abstract

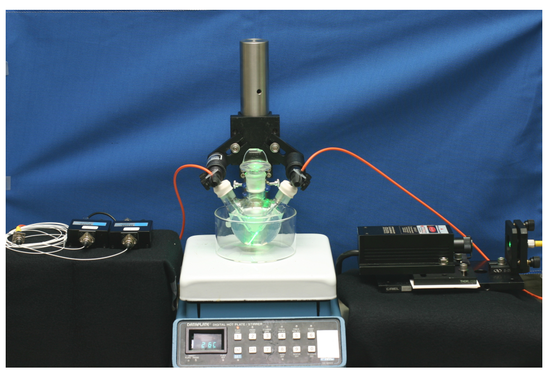
We describe a method for constructing a fiber optic based dynamic light scattering (DLS) instrument from commercially available components, without any need for customized parts. This approach, while providing good sensitivity and high accuracy, possesses several advantages not found in typical DLS instrumentation. It was found that aligning this instrument to obtain optimal detection efficiency can be completed in as little as a few minutes. Also, complications associated with light refraction at the sample cell interface are avoided. Small volumes (< 10 mL) can be measured, for example, by hanging a solution droplet from the fiber optic probe tips. In addition, use of fiber optic probes allows the beam path length to be as short as 1.6 mm while still measuring at 90º, which reduces the likelihood of multiple scattering. Finally, this approach is versatile, and can be incorporated into a wide variety of reaction and measurement platforms. The versatility of this DLS is demonstrated by integrating it into a standard 3-neck flask, thereby allowing, for instance, the progress of a Stöber synthesis of silica nanoparticles to be monitored. A battery-operated portable setup with submersible probes is also described and its performance is evaluated by measuring the temperature dependent swelling of poly(N-isopropyl acrylamide) latex microgel particles.

## Fiber optic based DLS setup




**A schematic representation of the instrument**

1 - 532 nm DPSS laser
2 - tilt stage with a fiber collimator
3 - adjustable probe holders
4 - submersible probe tips
5 - 50/50 single mode fiber splitter
6 - PMT photon counting modules
7 - correlator and personal computer
8 - small volume sample cell
9 - collimating GRIN lens at the end of a probe tip

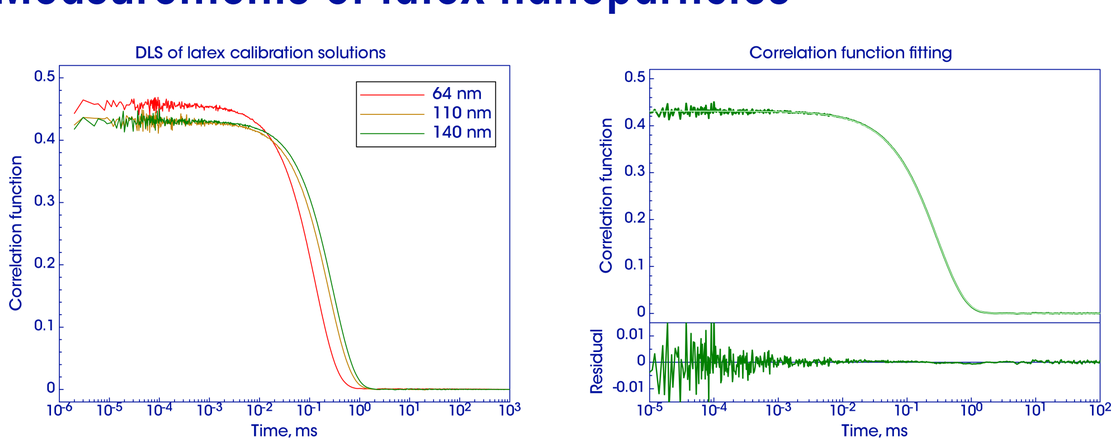


**A photograph of the instrument**

This image includes all components used to make DLS measurements including the detectors and the laser. The fiber probes are aligned inside a standard reaction flask during silica nanoparticles synthesis.

The instrument uses two identical fiber probes (OZ Optics, LPC-07 series singlemode fiber collimators) with tips that are immersed into the sample solution. Each tip has a stainless steel housing (1.58 mm diameter) with a gradient index (GRIN) lens secured inside. A single mode fiber end (numerical aperture 0.11) is pre-aligned against the GRIN lens, resulting in a collimated beam (full-angle beam divergence of 0.2º, 0.22 mm diameter). This beam diameter corresponds to an observation volume of 7 nL at a 90° scattering angle. The probes are mounted inside optical post holders at an angle, which is later precisely determined by calibration measurements, and their tips are positioned close to each other. A beam from a diode pumped solid state (DPSS) laser (Laserglow, LLS series, 532 nm, 125 mW, 2 mm diameter) is coupled to the FC-terminated fiber of the probe using an aspherical lens collimator (8 mm focal distance). The scattered light is collected by the second probe and directed through a 50/50 fiber splitter (OZ Optics, Fused-12 series) to two photomultiplier tube (PMT) detectors (Hamamatsu H7155) connected to a digital correlator (Correlator.com, Flex0201D/C).

## Measurements of latex nanoparticles




**Representative DLS correlation functions of monodisperse latex particles of three different sizes in water**

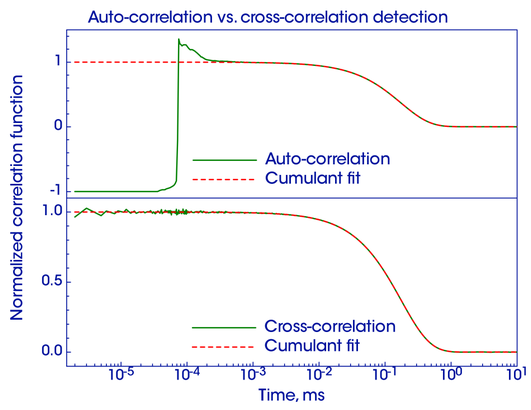
An important feature of this instrument is that it can be easily aligned. That is, optimal detection efficiency only requires that the lines of sight of the two probes fully intersect which can be achieved by one quick adjustment. Singlemode fibers inside the probes were pre-aligned and secured against GRIN lenses by the manufacturer, providing a diffraction limited collimated beam at a wavelength of 633 nm. This corresponds to a 0.2º (3.5 mrad) full-angle beam divergence. One measure of the quality of alignment is the spatial coherence factor (ß), which describes the instrument's ability to only collect light from the coherence volume. While detection efficiency was easily optimized, it was found that the probes used in this work yielded ß values of ca. 0.5 when used at 532 nm. When used at 633 nm, the ß value increased to 0.9.

### Evaluation of instrument accuracy using latex calibration standards [a]

| Particle size standards | Manufacturer specified size [b], nm | Zetasizer 3000 determined size [c], nm | Fiber optic DLS determined size [d], nm |
|---|---|---|---|
| Latex spheres (Polysciences) [e] | 107.6 ± 4.5 | 106.4 ± 0.6 | angle determination [f] |
| Latex spheres (Duke Scientific) [e] | 64 ± 3 | 64.1 ± 0.5 | 64.5 ± 0.3 |
| Carboxylated latex spheres (IDC) [g] | 110 ± 8 | 110.2 ± 0.7 | 109.2 ± 0.7 |
| Carboxylated spheres (IDC) [g] | 140 ± 12 | 141 ± 1 | 140 ± 1 |

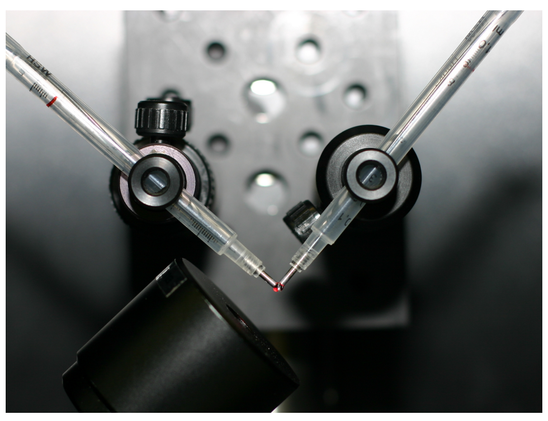
[a] Latex standards were diluted to the particle concentration $10^{10}$ mL$^{-1}$. For all DLS measurements acquisition time was 1 min, the average of 5 measurements and the standard deviation are reported. Cumulants method fits resulted in second order polydispersity indexes $\mu_2/G^2$ below 0.005 for all samples.
[b] Size determined by scanning electron microscopy.
[c] Malvern Zetasizer 3000 measurements were made using 1.5 mL sample volume in standard 1 cm spectroscopic cells at stabilized temperature 25 ºC.
[d] Fiber probe DLS measurements were made using probes immersed in 1 mL sample cell at room temperature (23.5 °C).
[e] Measured in deionized water.
[f] The scattering angle of 125° was determined by using the manufacturer specified size of 107.6 nm.
[g] Measured in pH 10 adjusted water.

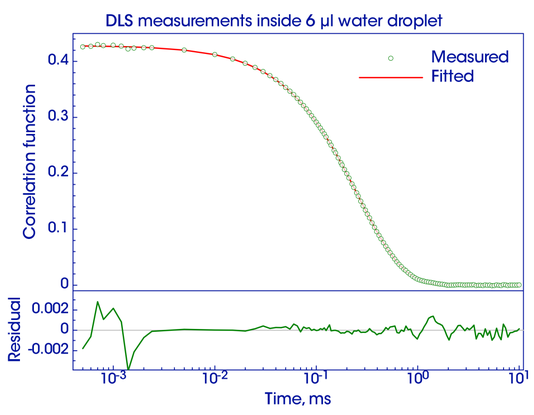
## Detector dead time and afterpulsing effects



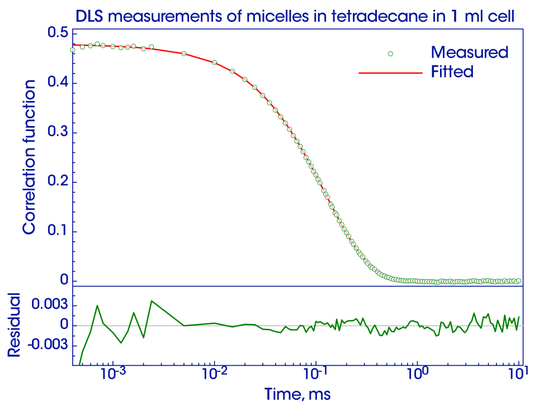

Auto- and cross-correlation functions are shown to demonstrate the impact of afterpulsing. Measurements were made on the 110 nm carboxylated latex spheres. Afterpulsing results in a rise in the autocorrelation below 800 ns. Furthermore, the pulse pair resolution of these PMTs (Hamamatsu H7155) is 70 ns. Below that time, the auto correlation goes to –1, reflecting a zero probability to observe a pulse within 70 ns of the previous one. Cross-correlation eliminates the impact of afterpulsing and pulse pair resolution in the correlated data.

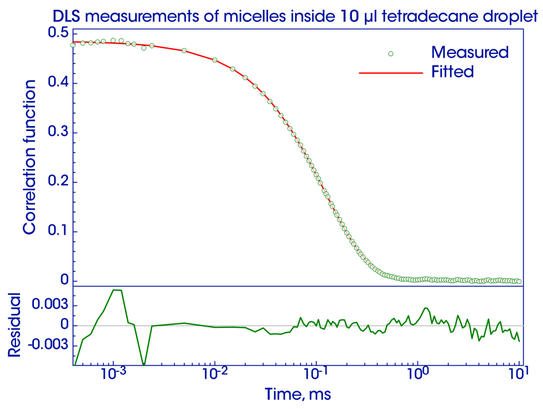
## Low volume DLS measurements





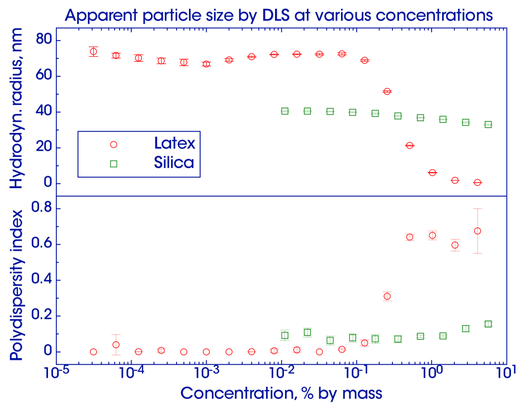

Another important advantage of this DLS instrument is its ability to characterize small sample volumes. Since no refraction occurs, small volumes can be measured at any angle. In contrast, most existing DLS instruments measure < 1 mL volumes only in square cuvettes at a 90° scattering angle, since small round cuvettes are too highly curved and introduce significant refraction. We demonstrates small sample volume measurements simply by hanging a 6 mL to 10 mL droplet of sample solution from the probe tips. The droplet volume was adjusted to direct the laser beam, partially reflected at the opposite side of the droplet, back to the laser probe. By controlling the reflections at the surface of the droplet, the coherence factor was not diminished.




A droplet suspended from the probe tips is susceptible to evaporation, which impacts the DLS measurement. Solvent evaporation from the surface of the droplet lowers the average solution temperature and leads to convective particle flow. Decreases in solution temperature slow particle diffusion, whereas convection can have the opposite effect of accelerating the correlation function decay. For water droplets, we found that the diffusion coefficient was slower than bulk solution measurements indicating that the impact of cooling was dominant. The discrepancy could be accounted for by consistently fitting the autocorrelation function with a temperature 3 °C below ambient. Measurements of block copolymer micelles in a non-volatile solvent, (tetradecane, boiling point = 270 °C) were unaffected by sample evaporation. Results from a hanging 10 mL droplet and a 1 mL sample volume were in excellent agreement.

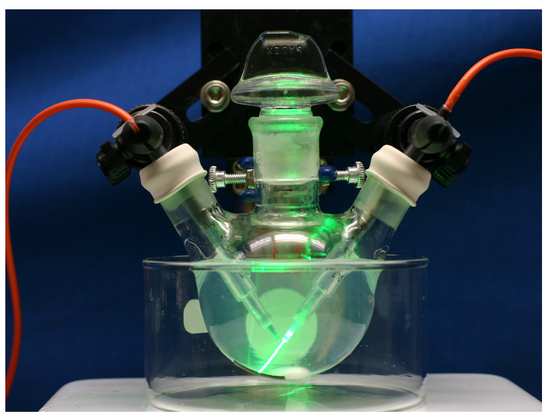
# Concentration dependence of DLS measurements

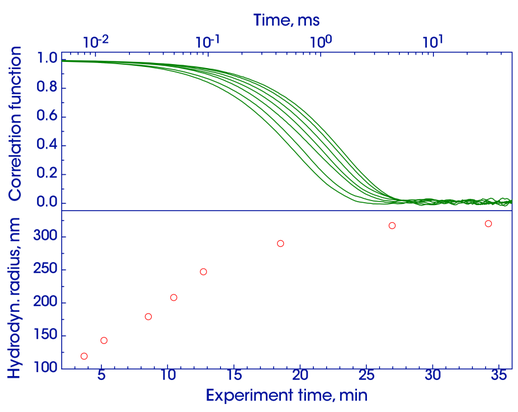



Fiber optic DLS measurements as a function of concentration are shown for 140 nm carboxylated polystyrene latex spheres at a scattering angle of 125° (circles), and 80 nm silica nanoparticles at a scattering angle of 90° (squares). Probes were positioned to minimize the optical path length (1.58 mm at 90°, 3.05 mm at 125°). The average and standard deviation of five 1 min long measurements are shown. The onset of multiple scattering abruptly occurs at ca. 0.2 % by mass for the aqueous polystyrene sample. The impact of multiple scattering is much less apparent in the aqueous silica solutions. The measured size deviates only 17 % for a concentration as high as 5.7 % by mass.

One limitation of DLS is that it normally can only measure dilute solutions. Overly concentrated samples exhibit multiple scattering, invalidating a key assumption used to interpret experimental results. Measurements were made with the fiber optic DLS instrument on aqueous polystyrene samples, and it was found that it exhibited an onset of multiple scattering at 0.2 % by mass. Polystyrene particles in water represent a rather extreme case in terms of refractive index contrast (1.59 vs. 1.33). Measurement of silica particles demonstrates the ability to measure higher concentrations when the refractive index mismatch is lower (1.46 vs. 1.33).

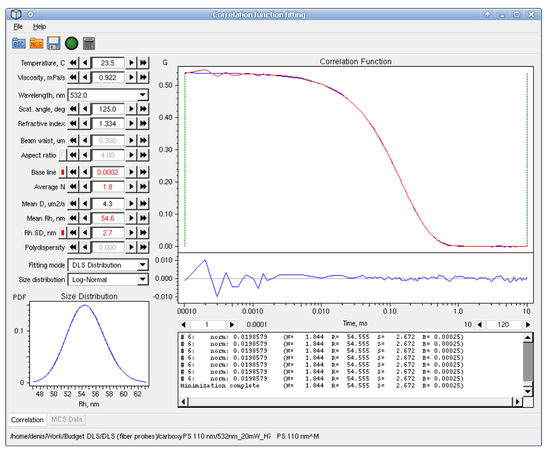
# Fiber optic DLS for particle synthesis monitoring





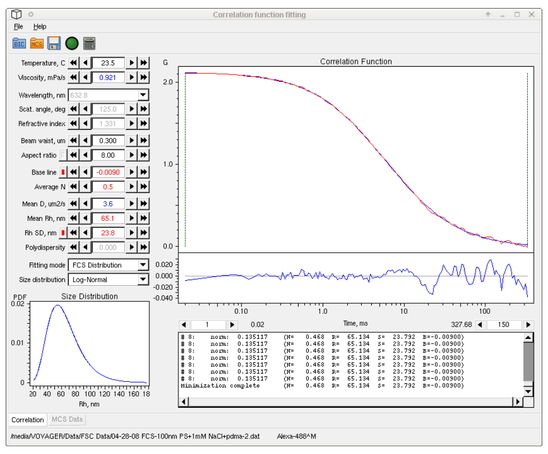

Another advantage of this approach to DLS is its versatility. To emphasize this point, the DLS is embedded into a standard three-neck flask. The probes are introduced though septa, allowing the reactor to remain sealed. The standard Stöber method was used to prepare silica nanoparticles, and their growth throughout the course of the reaction was monitored. Quantitative size determination could be made within 3 min of starting the reaction. Stirring was stopped 15 s prior to any measurements to avoid the influence stirring-induced particle motion would have on the measured autocorrelation function. Given the competing requirements of sample mixing during synthesis and the lack of stirring-induced particle motion during measurement, it is apparent that reaction monitoring is best suited for slow reactions. We found silica nanoparticles to grow to a size of 640 nm after approximately 27 min. Measurement of the diluted reaction product on a standard commercial instrument (Brookhaven Instruments BI200SM, 10 mm cuvette, 90° scattering angle) found a larger size (710 nm ± 8 nm). The apparent hydrodynamic radius of the undiluted product solution is underestimated due to the influence of multiple scattering. The discrepancy agrees with the concentration dependence of the apparent hydrodynamic radius shown above.

# Correlation function fitting




**A screenshot of DLS data fitting software suggesting log-normal particle size distribution**

Monodisperse latex particles (110 nm standard) demonstrate very narrow size distribution: the average hydrodynamic radius is 54.6 nm, the size distribution width is 2.7 nm.

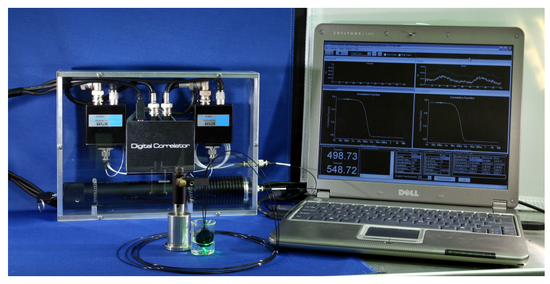



**A screenshot of FCS data fitting software suggesting log-normal particle size distribution**

Fluorescently labeled latex particles (110 nm standard) were coated with two layers of polymer: the average hydrodynamic radius is 65 nm, the size distribution width is 24 nm.

The fitting software used is written in C++, open source, cross-platform, and has no library dependencies. Currently two versions of this program are supported which work under Windows XP and Debian Linux. Fitting modes are quadratic cumulants and analytical unimodal size distributions, including log-normal and gamma distributions. The program can also fit correlation curves obtained from fluorescence correlation spectroscopy (FCS) measurements. The program is currently used to fit data acquired by the Brookhaven BI-9000AT correlator card, although the data importing routine could be easily extended to import data generated by other correlation cards. The program source code is distributed under GNU General Public License. Please contact Denis Pristinski (denis.pristinski@nist.gov) to obtain a copy of the program.

# Portable battery operated setup

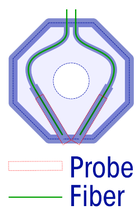




**A photograph of the portable instrument**

This image demonstrates a portable setup with a submersible fiber optic probe assembly.

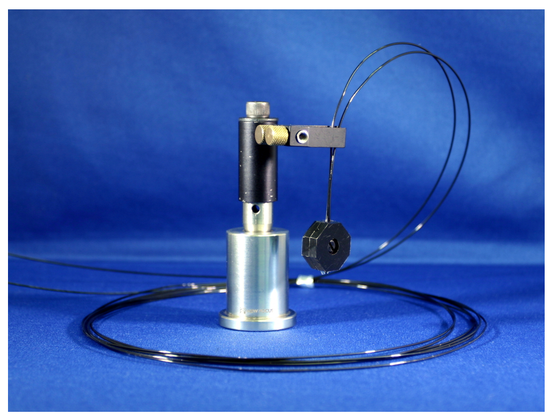
The instrument utilizes a battery operated laser (Laserglow Aries 200 mW, 532 nm) which is coupled to a singlemode fiber probe using an aspherical lens collimator (Thorlabs, 8 mm focal distance). The setup has two custom machined parts: a miniature aluminum tilt stage holding the aspherical lens and a plastic (derlin) clamp holding two GRIN lenses. All other components are the same as used with non-portable instrument described above. The digital correlator and PMT detectors are powered by laptop computer USB ports. Their combined power consumption depends on the photon count and typically is below 0.8 W (5 V, 160 mA). The 200 mW laser requires 3 W of electrical power (3 V, 940 mA) and runs on two C size batteries which last for about one hour. The instrument components are housed inside a box (25 × 18 × 4.5 cm) which has two FC receptacles for fiber probes mounted at its side.

## Submersible fiber optic probe assembly



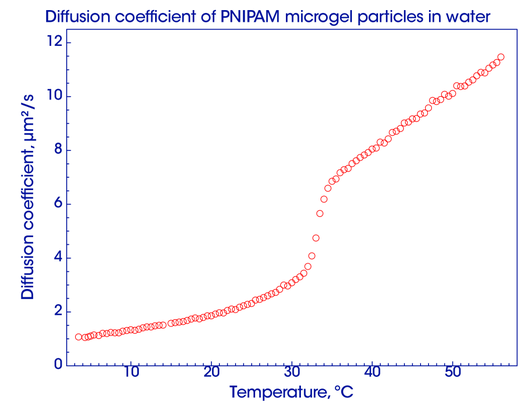

**A schematic drawing of the fiber probe clamp**

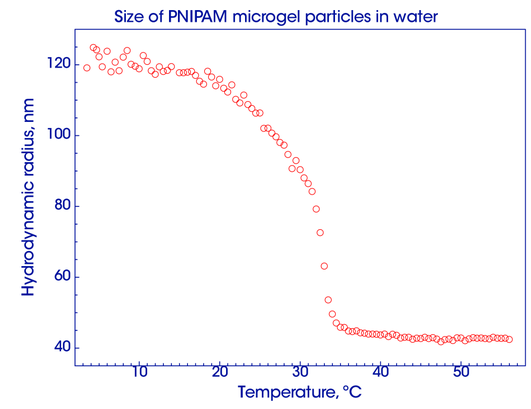
The clamp is 18 mm wide and consists of two matching halves, each one is CNC machined from 3 mm thick plastic. The clamp holds fiber probes aligned at 118°. This particular design was motivated by the requirement of minimum 6 mm bending radius of a singlemode fiber to avoid losses while maintaining an overall compact size. The clamp is secured with a plastic screw in its center.



Comparing the total photon count and the coherence factor of DLS measurements, it was found that the fiber optic probes secured inside the clamp perform as good as those mounted inside adjustable holders. This combination of the zero adjustment submersible probe assembly and singlemode fibers having negligible losses over long distances can significantly extend the list of DLS applications.

# The performance of submersible probe assembly




To demonstrate the capability of the portable instrument, it was used to characterize the swelling and collapse of poly(N-isopropyl acrylamide) (PNIPAM) latex microgel particles in water at the varying temperature. The PNIPAM particles were synthesized by a dispersion polymerization. The measurements were done inside a sealed 20 ml vial in a temperature stabilized water bath with the probe assembly immersed in the particle solution. The fiber optic probe assembly provided accurate results and was not affected by changing temperature from 0 to 60 ºC.

# Summary

A method for assembling a fiber optic based DLS instrument was presented. It was demonstrated that the accuracy and precision of the technique was not compromised by the choice of affordable parts. In addition, unique advantages of this type of DLS include simplified alignment, no refraction, as little as 6 µL sample volumes, and reduced likelihood of multiple scattering. With minimal customization, a portable dip-probe device can be made which could be used, for example, to evaluate the contents of an industrial reactor or a dialysis bag.The advantages of this DLS instrument are expected to make it valuable to many areas of research. Finally, given the importance of this technique in academic and industrial research and the low cost of this DLS instrument, it should be beneficial to incorporate it into undergraduate and graduate teaching laboratories.


## Acknowledgments

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